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(54) CATALYST FOR PURIFICATION OF EXHAUST GAS AND ITS PRODUCTION

(57)Abstract:
PURPOSE: To provide a catalyst having satisfactory purification activity even in the condition of a low temp. of exhaust gas and excellent in durability, as well.
CONSTITUTION: The objective catalyst has palladium allowed to coexist with a mixture of a perovskite type multiple oxide with a heat resistant oxide so that palladium is present at a higher concn. on the perovskite type multiple oxide than that on the heat resistant oxide. When the catalyst is produced, an aq. palladium salt soln. of ≤pH4 or >pH10 is carried on the above- perovskite type multiple oxide by impregnation or adsorption, the oxide is dried, calcined and dispersed in water together with the heat resistant oxide and the resulting slurry is dried and fired.

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

CLAIMS

[Claim(s)]

[Claim 1] It is the catalyst for emission gas purification characterized by for noble metals living together into the mixture of the perovskite mold multiple oxide and the heat-resistant oxide which are shown by general formula Ln1-xAxMO3 (the rare earth metal except Ce and A are transition metals, and Ln is [alkaline earth metal, or Ce and M] all one sort or two sorts or more, and 0< x<1), and said noble metals existing on said perovskite mold multiple oxide rather than said heat-resistant oxide top at high concentration.

[Claim 2] Said perovskite mold multiple oxide is a catalyst for emission gas purification according to claim 1 which has structure where the perovskite mold multiple oxide which dissolved noble metals was formed in the perimeter, by using as a nucleus the perovskite mold multiple oxide which does not contain noble metals.

[Claim 3] The catalyst for emission gas purification according to claim 1 or 2 which the oxide of noble metals or noble metals is distributing in the state of a particle.

[Claim 4] Noble metals are catalysts for emission gas purification according to claim 1, 2, or 3 which are one sort or two sorts or more of metals chosen from the group which consists of Pd, Pt, Ru, Rh, and Ir.

[Claim 5] Noble metals are catalysts for emission gas purification according to claim 4 which are Pd.

[Claim 6] General formula Ln1-xAxMO3 (the rare earth metal excluding [Ln] Ce, an alkaline earth metal excluding [A] Sr, or Ce and M are transition metals) All to one sort or two sorts or more, and the perovskite mold multiple oxide shown by 0< x<1 The manufacture approach of the catalyst for emission gas purification characterized by drying and calcinating after it makes the noble-metals salt water solution prepared by four or less support by sinking in or adsorption, pH distributes water with a heat-resistant oxide desiccation and after carrying out temporary quenching, and it considers as a slurry.

[Claim 7] General formula Ln1-xAxMO3 (alkaline earth metal, or Ce and M of the rare earth metal excluding [Ln] Ce and A are transition metals) All to one sort or two sorts or more, and the perovskite mold multiple oxide shown by 0< x<1 The manufacture approach of the catalyst for emission gas purification characterized by drying and calcinating after making the noble-metals salt water solution prepared so that pH might become larger than 10 support by sinking in or adsorption, distributing water with a heat-resistant oxide desiccation and after carrying out temporary quenching, and considering as a slurry.

[Translation done.]

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the catalyst for emission gas purification which shows purification activity also on the conditions that the exhaust gas temperature at the time of an idling etc. is low, and its manufacture approach in the catalyst for exhaust gas purification excellent in the purification capacity of a carbon monoxide (CO), a hydrocarbon (HC), and nitrogen oxide (NOx), especially the gasoline engine for automobiles, etc.
[0002]
[Description of the Prior Art] As a three way component catalyst for exhaust gas purification, the precious metal catalyst which supported noble metals, such as Pt, Rh, and Pd, is put in practical use by alumina support, and it is widely used for it. Moreover, utilization is expected as a cheap three way component catalyst for exhaust gas purification with which the multiple oxide which has the perovskite type structure which consists of a rare earth metal, an alkaline earth metal, and transition metals purifies CO, HC, and NOx (refer to JP,59-87046,A and JP,60-82138,A). Although CO and the purification capacity of HC are excellent, this perovskite mold multiple oxide is a little inferior in the purification capacity of NOx, and they are not enough to present practical use as a three way component catalyst for automobile exhaust. Then, in order to heighten the NOx purification capacity of a perovskite mold multiple oxide catalyst, also making noble metals live together is proposed (refer to JP,1-168343,A).
[0003]
[Problem(s) to be Solved by the Invention] Although these catalysts show the purification activity excellent in the conditions that exhaust gas temperature like [at the time of transit of an automobile] is high, they do not show purification activity sufficient on the conditions that the exhaust gas temperature at the time of an idling etc. is low. A catalyst which shows sufficient purification activity also on the conditions that such exhaust gas temperature is low, with exhaust gas toughening of regulations is desired. In order to raise the thermal resistance of a perovskite mold multiple oxide catalyst, it can consider making a heat-resistant oxide live together. When it is going to make palladium live together as noble metals into the mixture of a perovskite mold multiple oxide and heat-resistant oxide, after infiltrating a palladium salt water solution into the mixture of oxide, it is possible to calcinate. When the specific surface area of a perovskite mold multiple oxide uses for example, the Seria system multiple oxide as a heat-resistant oxide to 5-50m2/g and a large thing being 100m2/g, the specific surface area is large like 100-250m2/g. When a palladium salt water solution is infiltrated into the mixture of an oxide, the fine particles of each oxide are adsorbed in palladium with the surface coverage mostly proportional to specific surface area. That is, as for a heat-resistant oxide top, the noble metals for heightening NOx purification capacity are adsorbed by high concentration rather than a perovskite mold multiple oxide top.
[0004] In order to raise the property of both low-temperature activity and endurance, as for noble metals, such as palladium, it is desirable for high concentration to be adsorbed by the perovskite mold multiple oxide top. This invention aims at offering the manufacture approach for the catalyst for emission gas purification excellent also in endurance while it shows purification activity sufficient also on the conditions that exhaust gas temperature is low.
[0005]
[Means for Solving the Problem] With the catalyst for emission gas purification of this invention, noble metals live together into the mixture of the perovskite mold multiple oxide and the heat-resistant oxide which are shown by general formula Ln1-xAxMO3 (the rare earth metal except Ce and A are transition metals, and Ln is [alkaline earth metal, or Ce and M] all one sort or two sorts or more, anc 0< x<1), and said noble metals exist on said perovskite mold multiple oxide rather than said heat-resistant oxide top at high concentration. In the desirable mode, the perovskite mold multiple oxide is having structure where the perovskite mold multiple oxide which dissolved noble metals was formed in the perimeter, by using as a nucleus the perovskite mold multiple oxide which does not contain noble metals. When noble metals exist superfluously, the noble metals which were not able to dissolve are distributed in the state of a particle as a metal or an oxide. Noble metals are one sort or two sorts or more of metals chosen from the group which consists of Pd, Pt, Ru, Rh, and Ir, and especially Pd raises low-temperature purification activity and NOx purification activity, and is desirable.
[0006] Especially the class of heat-resistant oxide has the desirable multiple oxide which is not what is restricted and which is expressed with the general formulas (CeZrLn) O2 (rare earth metal excluding [Ln] Ce), such as O (CeZrY)2, O (CeZrLa)2, O (CeZrNd) 2, etc. besides CeO2 and O (CeZr)2. Moreover, since two are excelled in the effectiveness that the direction of CeOO(CeZr) 2 raises hot purification activity and it excels in the effectiveness that the direction of O2 raises hot purification activity further (CeZrLn), it is more desirable. Moreover, the thing (refer to JP,62-56322,A) containing at least one kind of metallic oxide chosen from the group whic makes the second cerium of oxidation a subject, for example, and becomes it from aluminum, Si, Zr, Th, and a rare earth metal element may be used.
[0007] In one mode of the manufacture approach of this invention, it is general formula Ln1-xAxMO3 (the rare earth metal excluding [Ln] Ce, an alkaline earth metal excluding [A] Sr, or Ce and M are transition metals). All are dried and calcinated after making it

support by sinking in or adsorption, making one sort or two sorts or more, and the perovskite mold multiple oxide in which it is shown by 0< x<1 distribute in water the noble-metals salt water solution with which pH was prepared by four or less with a heat-resistant oxide desiccation and after carrying out temporary quenching, and considering as a slurry. When pH is prepared and manufactured or less to four, a perovskite mold multiple oxide turns into an oxide with which the perovskite mold multiple oxide which dissolved noble metals enclosed the surroundings of it by using a perovskite mold multiple oxide as a nucleus. In the case of the manufacture approach which makes pH of a noble-metals salt water solution four or less As a water-soluble noble-metals salt, chlorides, such as PdCl2, PtCl2, and RuCl3.3H2O, Dinitro diamine salts of that a water solution indicates strong acid nature to be, such as nitrates, such as Pd (NO3)2, Ru (NO3)3, and Rh (NO3)3, Pd(NO2)2(NH3) 2, and Pt(NO2)2(NH3) 2, etc. are desirable.

[0008] In other modes of the manufacture approach of this invention, the perovskite mold multiple oxide shown by general formula Ln1-xAxMO3 (A contains Sr in this case) is made to support the noble-metals salt water solution prepared so that pH might become larger than 10 by sinking in or adsorption, and it dries and calcinates, after distributing water and considering as a slurry with the thermal-resistance oxide desiccation and after carrying out temporary quenching. In the case of the manufacture approach which makes pH of a noble-metals salt water solution larger than 10 Tetrapod amine palladium dichloride Pd(NH3)4Cl2 and tetra-amine palladium oxalate (NH3) (OH) Pd 4 [whether it prepares and uses so that aqueous ammonia and an acid may be added in basic water solutions, such as 2, and it may be set to pH>10, and] Nitrates, such as chlorides, such as PdCl2, PtCl2, and RuCl3.3H2O, and Pd (NO3)2, Ru (NO3)3, Rh (NO3)3, Or it prepares and uses so that aqueous ammonia may be added to aqueous acids, such as dinitro diamine salts, such as Pd (NO2)2(NH3) 2 and Pt(NO2)2(NH3) 2, and it may be set to pH>10.

[0009]

[Effect of the Invention] The catalyst of this invention shows the purification activity which was excellent to HC, CO, and NOx also in the low conditions whose exhaust gas temperature at the time of an idling etc. is about 100-200 degrees C. Moreover, while being able to use even an elevated temperature 900 degrees C or more including a heat-resistant oxide, it becomes a durable catalyst when noble metals effective in purification of NOx exist on a perovskite mold multiple oxide rather than the heat-resistant oxide top at high concentration.

[0010]

[Example]

(Example 1)

Procedure A : The preparation approach of manufacture approach perovskite mold multiple oxide (La0.8Ce0.2) (Co0.4Fe0.6) O3 powder of perovskite mold multiple oxide crystal powder is explained. 103.9g of lanthanum nitrates, 26.1g of cerium nitrates, 34.9g of cobalt nitrates, and 0.3l. of water solutions which dissolved 72.7g of iron nitrate in pure water were prepared. Next, 0.5l. of water solutions which dissolved 50g of sodium carbonates as a neutralization coprecipitater was prepared. The neutralization coprecipitater was dropped at the previous water solution, and the coprecipitate was obtained. The vacuum drying was carried out, after rinsing the coprecipitate enough and filtering it. This was ground after baking in 3-hour atmospheric air at 600 degrees C, and it calcinated in 3-hour atmospheric air at 800 degrees C after that, and ground further, and the powder of O(Co(La0.8Ce0.2)0.4Fe0.6) 3 was produced.

[0011] cerium oxide powder of a commercial high specific surface area [oxide / which is used as a manufacture co-catalyst of a procedure B thermal-resistance oxide / heat-resistant] : (CeO2 specific-surface-area 170m2/g —) 99.9% of purity and TREO(all rare earth oxides)111.9g are prepared. To this, 147.9g (contained 25.0% of the weight by ZrO2 conversion in liquid density 1.51 and liquid) of oxy-zirconium-nitrate (ZrO2 (NO3)) water solutions, And 26.0g (contained 21.7% of the weight by 2OY3 conversion in liquid density 1.62 and liquid) of nitric-acid yttrium (Y(NO3) 3) water solutions was added, and it dried in 10-hour atmospheric air at 110 degrees C, having agitated well and mixing. Then, baking was performed at 600 degrees C in atmospheric air for 3 hours, and about 150g of O(Ce0.65Zr 0.30Y0.05)2 multiple oxides was obtained.

[0012]

Procedure C : The palladium nitrate solution (Pd concentration 4.4wt%) 25 weight section and the pure-water 50 weight section were mixed so that it might become the 1.1 weight section by part for the content Pd of Pd to perovskite powder, and pH of liquid was prepared to 1.8. After adding the pure-water 20 weight section to the O(Co(La0.8Ce0.2)0.4Fe0.6) 3 perovskite mold multiple oxide powder 98.9 weight section manufactured in Procedure A and agitating enough, the above-mentioned Pd salt water solution 75 weight section adjusted to pH1.8 was infiltrated, and it agitated enough, and held for 30 minutes at 40 degrees C. Then, after drying at 120 degrees C for 12 hours and calcinating at 600 degrees C in air for 3 hours, continuing churning, the agate mortar ground and a 180-micrometer mesh was passed. Pd added to the perovskite powder 98.9 weight section is equivalent to the 1.1 weight section by part for a metal.

[0013] Procedure D : Slurry coat (support)

The heat-resistant oxide powder which manufactured Pd content perovskite powder obtained in Procedure A in 50 weight sections and Procedure B 50 weight sections, A ceria sol (solid content 10wt%) 50 weight sections (solid content 5 weight sections), And it mixed, while the 58.7 weight sections were added and the ball mill ground pure water for 12 hours so that total solids might become 50wt(s)% about a zirconia sol (solid content 30wt%) at the 3.3 weight sections (solid content 1 weight section), and the slurry was obtained. After making the slurry flow into a KOZE light honeycomb, the excessive slurry was blown off by airstream and homogeneity was coated. The honeycomb behind a slurry coat was dried at 120 degrees C for 12 hours, in air, it calcinated at 600 degrees C for 3 hours, and the honeycomb-like sample was obtained.

[0014] Procedure E : The same palladium nitrate solution (Pd concentration 4.4wt%) 12.5 weight section as what was used for the re-addition pan of Pd in Procedure C was mixed with the pure-water 50 weight section, and pH of liquid was prepared to 1.8. After having immersed the honeycomb-like sample in this solution whole quantity, holding at 40 degrees C for 2 hours, making Pd adsorb and making it dry at 120 degrees C for 12 hours, in air, it calcinated at 600 degrees C for 3 hours, and the catalyst sample of an example 1 was obtained.

[0015] The analysis result by EPMA (electron probe microanalyzer) of this catalyst sample is shown in the photograph of drawing 1 . With a photograph, an image is an image by the scanning electron microscope (SEM), a big black particle is a perovskite mold multiple

oxide, and magnitude is about 10 micrometers. A small white particle is a heat-resistant oxide particle, and magnitude is about 3 micrometers. Rhine which crosses a center in a longitudinal direction is criteria Rhine which shows the location which performed line analysis, and the wave expresses Pd concentration on the analytical line. According to the result of this photograph, Pd concentration of the periphery section of a perovskite mold multiple oxide particle is high [else].

[0016] (Example 2) The palladium nitrate solution used in the procedure E of an example 1 was changed into the tetra-ammine palladium nitrate (Pd concentration 4.6wt%), and the catalyst sample of an example 2 was obtained by actuation like the example 1 except having added the aqueous ammonia 50 weight section and having set pH to 13.0.

[0017] (Example 3) The powder which added the amount which the palladium nitrate solution used in the procedure C of an example 1 was changed into the tetra-ammine palladium nitrate (Pd concentration 4.6wt%), and also is equivalent to the 1.1 weight section in Pd to the perovskite mold multiple oxide powder 98.9 weight section by the same actuation as procedure A-C of an example 1 with a part for a metal was obtained. Then, the catalyst sample of an example 3 was obtained by the same actuation as an example 1.

[0018] (Example 4) Both changing into the tetra-ammine palladium nitrate (Pd concentration 4.6wt%) the palladium nitrate solution used in the palladium nitrate solution and Procedure E which were used in the procedure C of an example 1, others obtained the catalyst sample of an example 4 like the example 1.

[0019] (Example 5) In the procedure C of an example 1, 50 weight sections were measured so that it might become the 2.2 weight sections by part for Pd about a palladium nitrate solution, and the catalyst sample of an example 5 was obtained by the same actuation as an example 1 except having skipped Procedure E.

[0020] (Example 6) In the procedure C of an example 1, the palladium nitrate solution was replaced with the tetra-ammine palladium nitrate (Pd concentration 4.6wt%), the 47.8 weight sections were measured so that it might become the 2.2 weight sections by part for Pd, and the aqueous ammonia 50 weight section was added, it was referred to as pH=13.0, and the catalyst sample of an example 6 was obtained by the same actuation as an example 1 except having skipped Procedure E.

[0021] (Example 7) Replacing with O(Co(La0.8Sr0.2)0.4Fe0.6)3 powder perovskite mold multiple oxide (La0.8Ce0.2) (Co0.4Fe0.6) O3 powder used in the example 4, others obtained the catalyst sample of an example 7 by the same actuation as an example 4.

[0022] (Example 8) Replacing with O(Co(La0.8Sr0.2)0.4Fe0.6)3 powder perovskite mold multiple oxide (La0.8Ce0.2) (Co0.4Fe0.6) O3 powder used in the example 6, others obtained the catalyst sample of an example 8 by the same actuation as an example 6.

[0023] (Example 9) Replacing with La0.8Ce0.2CoO3 powder perovskite mold multiple oxide (La0.8Ce0.2) (Co0.4Fe0.6) O3 powder used in the example 5, others obtained the catalyst sample of an example 9 by the same actuation as an example 5.

[0024] (Example of a comparison) 2OPt-Rh/aluminum3 catalyst which is a catalyst for automobiles already put in practical use was made into the catalyst sample of the example of a comparison. The Pt-Rh content was the 0.43 weight section. The presentation of an example and the example of a comparison is shown in Table 1, and the measurement result of each catalytic activity is shown in Table 2.

[0025]

[Table 1]

	ペロブスカイト型複合酸化物	Ｐｄ含有量 (手順Ｃ)	溶液ｐＨ (手順Ｃ)	耐熱性酸化物	溶液ｐＨ (手順Ｅ)	総Ｐｄ量
実施例１	$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔0.55〕	1.8	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	1.8	Pd〔1.1〕
実施例２	$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔0.55〕	1.8	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	13.0	Pd〔1.1〕
実施例３	$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔0.55〕	13.0	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	1.8	Pd〔1.1〕
実施例４	$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔0.55〕	13.0	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	13.0	Pd〔1.1〕
実施例５	$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔1.1〕	1.8	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	―	Pd〔1.1〕
実施例６	$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔1.1〕	13.0	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	―	Pd〔1.1〕
実施例７	$(La_{0.8}Sr_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔0.55〕	13.0	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	13.0	Pd〔1.1〕
実施例８	$(La_{0.8}Sr_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔1.1〕	13.0	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	―	Pd〔1.1〕
実施例９	$(La_{0.8}Ce_{0.2})CoO_3$〔50〕	〔1.1〕	1.8	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	―	Pd〔1.1〕
比較例				γ-Al_2O_3〔100〕	1.8	Pt-Rh〔0.43〕

〔　〕内の数値は重量部を表わす。

[0026]
[Table 2]

	初期５０％浄化温度（℃）			耐久後５０％浄化温度（℃）		
	ＣＯ	ＨＣ	ＮＯ	ＣＯ	ＨＣ	ＮＯ
実施例１	１３８	１５６	１５５	２３１	２３６	２２０
実施例２	１３１	１５１	１５１	２２０	２２６	２１８
実施例３	１５０	１６７	１６９	２３２	２３７	２２３
実施例４	１４１	１６４	１７０	２２６	２３３	２１８
実施例５	１３８	１６２	１５２	２１２	２２４	２１４
実施例６	１３２	１６６	１６８	２３１	２４０	２１６
実施例７	１３４	１５５	１４８	２１８	２３１	２２５
実施例８	１３０	１６０	１５５	２２７	２４１	２３４
実施例９	１２９	１５４	１３７	２３６	２４６	２４８
比較例	１９３	２０８	１９８	２６３	２７６	２５９

[0027] Measurement and the durability test of catalytic activity were performed as follows.
Activity was measured for each sample supported by the measurement honeycomb-like (number of cels 400-/inch 2) cordierite support (the diameter of 30mm, die length of 50mm) of catalytic activity by the following model gas. The inlet gas temperature to a catalyst shows gas temperature, it carries out a temperature up from a room temperature, and makes purification temperature temperature to which each of NO, CO, and HC (C3H6+C3H8) fell to 50% of initial concentration 50%. Moreover, rich gas and lean gas were switched for every second, respectively. Space velocity (SV) of the gas stream which passes along a catalyst was made into 30,000-/time amount.
[0028]
Rich gas Lean gas CO 2.6 % 0.7 % HC (C1 conversion concentration) 0.19% 0.19% H2 0.87% 0.23% CO2 8 % 8 % NO 0.17% 0.17% O2 0.65% 1.8 % H2O 10% 10 % N2 Remainder Remainder [0029] The rich gas and lean gas of the durability test above were switched every 5 seconds, it repeated at 900 degrees C for 30 minutes, the cycle of 30 minutes was repeated 15 times at 750 degrees C, and the durability test was performed. Catalytic activity was measured by the aforementioned approach also after the durability test. 50% purification temperature is low after durability, and high in the example of a comparison to it so that clearly from the result of Table 2. [in / at each example / the first stage]

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the microphotography in which a metal presentation and palladium distribution of the catalyst of an example are shown.

[Translation done.]

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最終頁に続く

(54)【発明の名称】　排ガス浄化用触媒及びその製造方法

(57)【要約】
【目的】　排ガス温度が低い条件でも十分な浄化活性を示し、耐久性も優れたものとする。
【構成】　ペロブスカイト型複合酸化物と耐熱性酸化物との混合物にパラジウムが共存し、かつパラジウムは耐熱性酸化物上よりもペロブスカイト型複合酸化物上に高濃度に存在するようにする。その製造方法では、ペロブスカイト型複合酸化物に、ｐＨが４以下又は１０より大きく調製されたパラジウム塩水溶液を含浸又は吸着により担持させ、乾燥及び仮焼させた後、耐熱性酸化物とともに水に分散させてスラリーとした後、乾燥及び焼成する。

図面代用写真

写　真

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【特許請求の範囲】

【請求項１】 一般式$Ln_{1-x}A_xMO_3$（ＬｎはＣｅを除く希土類金属、Ａはアルカリ土類金属又はＣｅ、Ｍは遷移金属で、いずれも１種又は２種以上、０＜ｘ＜１）で示されるペロブスカイト型複合酸化物と耐熱性酸化物との混合物に貴金属が共存し、かつ前記貴金属は前記耐熱性酸化物上よりも前記ペロブスカイト型複合酸化物上に高濃度に存在していることを特徴とする排ガス浄化用触媒。

【請求項２】 前記ペロブスカイト型複合酸化物は貴金属を含まないペロブスカイト型複合酸化物を核としてその周囲に貴金属を固溶したペロブスカイト型複合酸化物が形成された構造をしている請求項１に記載の排ガス浄化用触媒。

【請求項３】 貴金属又は貴金属の酸化物が微粒子状態で分散している請求項１又は２に記載の排ガス浄化用触媒。

【請求項４】 貴金属はＰｄ，Ｐｔ，Ｒｕ，Ｒｈ及びＩｒからなる群より選ばれた１種又は２種以上の金属である請求項１，２又は３に記載の排ガス浄化用触媒。

【請求項５】 貴金属はＰｄである請求項４に記載の排ガス浄化用触媒。

【請求項６】 一般式$Ln_{1-x}A_xMO_3$（ＬｎはＣｅを除く希土類金属、ＡはＳｒを除くアルカリ土類金属又はＣｅ、Ｍは遷移金属で、いずれも１種又は２種以上、０＜ｘ＜１）で示されるペロブスカイト型複合酸化物に、ｐＨが４以下に調製された貴金属塩水溶液を含浸又は吸着により担持させ、乾燥及び仮焼させた後、耐熱性酸化物とともに水に分散させてスラリーとした後、乾燥及び焼成することを特徴とする排ガス浄化用触媒の製造方法。

【請求項７】 一般式$Ln_{1-x}A_xMO_3$（ＬｎはＣｅを除く希土類金属、Ａはアルカリ土類金属又はＣｅ、Ｍは遷移金属で、いずれも１種又は２種以上、０＜ｘ＜１）で示されるペロブスカイト型複合酸化物に、ｐＨが１０より大きくなるように調製された貴金属塩水溶液を含浸又は吸着により担持させ、乾燥及び仮焼させた後、耐熱性酸化物とともに水に分散させてスラリーとした後、乾燥及び焼成することを特徴とする排ガス浄化用触媒の製造方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は一酸化炭素（ＣＯ）、炭化水素（ＨＣ）及び酸化窒素（ＮＯｘ）の浄化能力に優れた排気ガス浄化用触媒、特に自動車用ガソリンエンジンなどにおいて、アイドリング時などの排ガス温度が低い条件でも浄化活性を示す排ガス浄化用触媒と、その製造方法に関するものである。

【０００２】

【従来の技術】排気ガス浄化用三元触媒としてはアルミ

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ナ担体にＰｔ、Ｒｈ、Ｐｄなどの貴金属を担持した貴金属触媒が実用化されて広く使用されている。また、希土類金属、アルカリ土類金属及び遷移金属から構成されるペロブスカイト型構造を有する複合酸化物は、ＣＯ、ＨＣ及びＮＯｘを浄化する安価な排気ガス浄化用三元触媒として実用化が期待されている（特開昭５９－８７０４６号公報、特開昭６０－８２１３８号公報参照）。このペロブスカイト型複合酸化物はＣＯ、ＨＣの浄化能力は優れているが、ＮＯｘの浄化能力がやや劣っており、自動車排ガス用の三元触媒として実用に供するには十分でない。そこで、ペロブスカイト型複合酸化物触媒のＮＯｘ浄化能力を高めるために、貴金属を共存させることも提案されている（特開平１－１６８３４３号公報参照）。

【０００３】

【発明が解決しようとする課題】これらの触媒は、自動車の走行時のような排ガス温度が高い条件では優れた浄化活性を示すが、アイドリング時などの排ガス温度が低い条件では十分な浄化活性を示さない。排ガス規制強化にともなってそのような排ガス温度が低い条件でも十分な浄化活性を示す触媒が望まれている。ペロブスカイト型複合酸化物触媒の耐熱性を高めるために、耐熱性酸化物を共存させることが考えられる。ペロブスカイト型複合酸化物と耐熱性酸化物との混合物に貴金属としてパラジウムを共存させようとした場合、酸化物の混合物にパラジウム塩水溶液を含浸させた後、焼成することが考えられる。ペロブスカイト型複合酸化物の比表面積は５～５０m^2／ｇ、大きいものでも１００m^2／ｇであるのに対し、耐熱性酸化物として例えばセリア系複合酸化物を用いるとその比表面積は１００～２５０m^2／ｇというように大きい。パラジウム塩水溶液を酸化物の混合物に含浸させた場合、ほぼ比表面積に比例した吸着率でそれぞれの酸化物の粉体にパラジウムが吸着される。つまり、ＮＯｘ浄化能力を高めるための貴金属はペロブスカイト型複合酸化物上よりも耐熱性酸化物上により高濃度に吸着される。

【０００４】低温活性と耐久性の両方の特性を向上させるためには、パラジウムなどの貴金属はペロブスカイト型複合酸化物上により高濃度に吸着されることが望ましい。本発明は排ガス温度が低い条件でも十分な浄化活性を示すとともに、耐久性にも優れた排ガス浄化用触媒と、その製造方法を提供することを目的とするものである。

【０００５】

【課題を解決するための手段】本発明の排ガス浄化用触媒では、一般式$Ln_{1-x}A_xMO_3$（ＬｎはＣｅを除く希土類金属、Ａはアルカリ土類金属又はＣｅ、Ｍは遷移金属で、いずれも１種又は２種以上、０＜ｘ＜１）で示されるペロブスカイト型複合酸化物と耐熱性酸化物との混合物に貴金属が共存し、かつ前記貴金属は前記耐熱性酸

化物上よりも前記ペロブスカイト型複合酸化物上に高濃度に存在している。好ましい態様では、ペロブスカイト型複合酸化物は、貴金属を含まないペロブスカイト型複合酸化物を核としてその周囲に貴金属を固溶したペロブスカイト型複合酸化物が形成された構造をしている。貴金属が過剰に存在した場合、固溶しきれなかった貴金属は、金属又は酸化物として微粒子状態で分散する。貴金属はＰｄ，Ｐｔ，Ｒｕ，Ｒｈ及びＩｒからなる群より選ばれた１種又は２種以上の金属であり、特にＰｄは低温浄化活性とＮＯｘ浄化活性を向上させるものであり好ましい。

【０００６】耐熱性酸化物の種類は特に制限されるものではない、例えば、CeO_2，（ＣｅＺｒ）O_2の他、（ＣｅＺｒＹ）O_2，（ＣｅＺｒＬａ）O_2，（ＣｅＺｒＮｄ）O_2など、一般式（ＣｅＺｒＬｎ）O_2（ＬｎはＣｅを除く希土類金属）で表わされる複合酸化物が好ましい。また、CeO_2よりは（ＣｅＺｒ）O_2の方が高温における浄化活性を高める効果に優れ、更に（ＣｅＺｒＬｎ）O_2の方が高温における浄化活性を高める効果に優れているので、より好ましい。また、例えば酸化第二セリウムを主体とし、それにＡｌ，Ｓｉ，Ｚｒ，Ｔｈ及び希土類金属元素よりなる群から選ばれた少なくとも１種類の金属酸化物を含んだもの（特開平６２－５６３２２号公報参照）でもよい。

【０００７】本発明の製造方法の一態様では、一般式$Ln_{1-x}A_xMO_3$（ＬｎはＣｅを除く希土類金属、ＡはＳｒを除くアルカリ土類金属又はＣｅ、Ｍは遷移金属で、いずれも１種又は２種以上、$0<x<1$）で示されるペロブスカイト型複合酸化物に、ｐＨが４以下に調製された貴金属塩水溶液を含浸又は吸着により担持させ、乾燥及び仮焼させた後、耐熱性酸化物とともに水に分散させてスラリーとした後、乾燥及び焼成する。ｐＨを４以下に調製して製造した場合には、ペロブスカイト型複合酸化物は、ペロブスカイト型複合酸化物を核としてその周りを貴金属を固溶したペロブスカイト型複合酸化物が取り囲んだ酸化物となる。貴金属塩水溶液のｐＨを４以下とする製造方法の場合は、水溶性貴金属塩としては$PdCl_2$、$PtCl_2$、$RuCl_3\cdot 3H_2O$などの塩化物、$Pd(NO_3)_2$、$Ru(NO_3)_3$、$Rh(NO_3)_3$などの硝酸塩、$Pd(NO_2)_2(NH_3)_2$、$Pt(NO_2)_2(NH_3)_2$などのジニトロジアミン塩など、水溶液が強酸性を示すものが好ましい。

【０００８】本発明の製造方法の他の態様では、一般式$Ln_{1-x}A_xMO_3$（この場合、ＡはＳｒを含む）で示されるペロブスカイト型複合酸化物に、ｐＨが１０より大きくなるように調製された貴金属塩水溶液を含浸又は吸着により担持させ、乾燥及び仮焼させた後、耐熱性酸化物とともに水に分散させてスラリーとした後、乾燥及び焼成する。貴金属塩水溶液のｐＨを１０より大きくする製造方法の場合は、テトラアミンパラジウムジクロライド$Pd(NH_3)_4Cl_2$やテトラアミンパラジウム水酸塩$Pd(NH_3)_4(OH)_2$などの塩基性水溶液にアンモニア水や酸を添加して$pH>10$になるように調製して用いるか、$PdCl_2$、$PtCl_2$、$RuCl_3\cdot 3H_2O$などの塩化物、$Pd(NO_3)_2$、$Ru(NO_3)_3$、$Rh(NO_3)_3$などの硝酸塩、又は$Pd(NO_2)_2(NH_3)_2$、$Pt(NO_2)_2(NH_3)_2$などのジニトロジアミン塩などの酸性水溶液にアンモニア水を添加して$pH>10$になるように調製して用いる。

【０００９】

【発明の効果】本発明の触媒はアイドリング時などの排ガス温度が１００～２００℃程度の低い条件においてもＨＣ，ＣＯ，ＮＯｘに対して優れた浄化活性を示す。また、耐熱性酸化物を含んで９００℃以上の高温でも使用できるとともに、ＮＯｘの浄化に有効な貴金属が耐熱性酸化物上よりもペロブスカイト型複合酸化物上に高濃度に存在していることにより耐久性のある触媒となる。

【００１０】

【実施例】

（実施例１）

手順Ａ　：　ペロブスカイト型複合酸化物結晶粉末の製造方法

ペロブスカイト型複合酸化物$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$粉末の調製方法を説明する。硝酸ランタン１０３.９ｇ、硝酸セリウム２６.１ｇ、硝酸コバルト３４.９ｇ、硝酸鉄７２.７ｇを純水に溶解した水溶液０.３リットルを用意した。次に、中和共沈剤として炭酸ナトリウム５０ｇを溶解した水溶液０.５リットルを用意した。中和共沈剤を先の水溶液に滴下し、共沈物を得た。その共沈物を十分水洗し、濾過した後、真空乾燥した。これを６００℃で３時間大気中で焼成後、粉砕し、その後、８００℃で３時間大気中で焼成を行ない、さらに粉砕し、$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$の粉末を作製した。

【００１１】手順Ｂ　：　耐熱性酸化物の製造

助触媒として用いる耐熱性酸化物は市販の高比表面積の酸化セリウム粉末（CeO_2比表面積１７０m^2／ｇ、純度９９.９％／ＴＲＥＯ（全希土類酸化物））１１１.９ｇを用意し、これにオキシ硝酸ジルコニウム$(ZrO(NO_3)_2)$水溶液（液比重１.５１、液中にZrO_2換算で２５.０重量％含まれる）１４７.９ｇ、及び硝酸イットリウム$(Y(NO_3)_3)$水溶液（液比重１.６２、液中にY_2O_3換算で２１．７重量％含まれる）２６．０ｇを加え、よく撹拌して混合しながら１１０℃で１０時間大気中で乾燥した。その後、大気中で６００℃で３時間焼成を行ない、$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$複合酸化物を約１５０ｇ得た。

【００１２】

手順Ｃ　：　ペロブスカイト粉末へのＰｄの含有

Ｐｄ分で１．１重量部となるように硝酸パラジウム溶液

（Ｐｄ濃度４．４ｗｔ％）２５重量部と純水５０重量部とを混合し、液のｐＨを１．８に調製した。手順Ａで製造した$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$ペロブスカイト型複合酸化物粉末９８．９重量部に純水２０重量部を加えて十分撹拌した後、ｐＨ１．８に調整した上記のＰｄ塩水溶液７５重量部を含浸させて十分撹拌し、４０℃で３０分間保持した。その後、撹拌を続けながら１２０℃で１２時間乾燥し、空気中で６００℃で３時間焼成した後、めのう乳鉢にて粉砕し、１８０μｍのメッシュを通過させた。ペロブスカイト粉末９８．９重量部に対して添加したＰｄは金属分で１．１重量部に相当する。

【００１３】手順Ｄ　：　スラリーコート（担持）
手順Ａで得たＰｄ含有ペロブスカイト粉末を５０重量部、手順Ｂで製造した耐熱性酸化物粉末を５０重量部、セリアゾル（固形分１０ｗｔ％）を５０重量部（固形分では５重量部）、及びジルコニアゾル（固形分３０ｗｔ％）を３．３重量部（固形分では１重量部）に、全固形分が５０ｗｔ％となるように純水を５８．７重量部を加え、ボールミルにて１２時間粉砕しながら混合してスラリーを得た。そのスラリーをコーゼライトハニカムに流入させた後、余剰のスラリーを空気流で吹き払い、均一にコーティングした。スラリーコート後のハニカムを１２０℃で１２時間乾燥し、空気中にて６００℃で３時間焼成してハニカム状サンプルを得た。

【００１４】手順Ｅ　：　Ｐｄの再添加
さらに、手順Ｃで用いたものと同じ硝酸パラジウム溶液（Ｐｄ濃度４．４ｗｔ％）１２．５重量部を純水５０重量部と混合し、液のｐＨを１．８に調製した。この溶液全量にハニカム状サンプルを浸漬し、４０℃で２時間保持してＰｄを吸着させた後、１２０℃で１２時間乾燥させた後、空気中にて６００℃で３時間焼成して実施例１の触媒試料を得た。

【００１５】この触媒試料のＥＰＭＡ（電子線マイクロアナライザー）による分析結果を図１の写真に示す。写真で、画像は走査型電子顕微鏡（ＳＥＭ）による像であり、黒い大きな粒子はペロブスカイト型複合酸化物で、大きさは約１０μｍである。白い小さな粒子は耐熱性酸化物粒子で、大きさは約３μｍである。中央を横方向に横切るラインは線分析を行なった位置を示す基準ラインであり、波形は分析線上でのＰｄ濃度を表わしている。この写真の結果によれば、ペロブスカイト型複合酸化物粒子の外周部のＰｄ濃度が他に比べて高くなっている。

【００１６】（実施例２）実施例１の手順Ｅで用いた硝酸パラジウム溶液をテトラアンミンパラジウム硝酸塩（Ｐｄ濃度４．６ｗｔ％）に変え、アンモニア水５０重量部を加えてｐＨを１３．０とした以外は、実施例１と同様に操作により実施例２の触媒試料を得た。

【００１７】（実施例３）実施例１の手順Ｃで用いた硝酸パラジウム溶液をテトラアンミンパラジウム硝酸塩（Ｐｄ濃度４．６ｗｔ％）に変えた他は、実施例１の手順Ａ～Ｃと同様の操作にて、ペロブスカイト型複合酸化物粉末９８．９重量部に対してＰｄを金属分で１．１重量部に相当する量を添加した粉末を得た。その後、実施例１と同様の操作により、実施例３の触媒試料を得た。

【００１８】（実施例４）実施例１の手順Ｃで用いた硝酸パラジウム溶液及び手順Ｅで用いた硝酸パラジウム溶液を、ともにテトラアンミンパラジウム硝酸塩（Ｐｄ濃度４．６ｗｔ％）に変え、他は実施例１と同様にして実施例４の触媒試料を得た。

【００１９】（実施例５）実施例１の手順Ｃにおいて、硝酸パラジウム溶液をＰｄ分で２．２重量部となるように５０重量部を計量し、手順Ｅを省いた以外は実施例１と同様の操作により、実施例５の触媒試料を得た。

【００２０】（実施例６）実施例１の手順Ｃにおいて、硝酸パラジウム溶液をテトラアンミンパラジウム硝酸塩（Ｐｄ濃度４．６ｗｔ％）に代え、Ｐｄ分で２．２重量部となるように４７．８重量部を計量し、アンモニア水５０重量部を加えてｐＨ＝１３．０とし、手順Ｅを省いた以外は、実施例１と同様の操作により実施例６の触媒試料を得た。

【００２１】（実施例７）実施例４で用いたペロブスカイト型複合酸化物$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$粉末を$(La_{0.8}Sr_{0.2})(Co_{0.4}Fe_{0.6})O_3$粉末に代え、他は実施例４と同様の操作により実施例７の触媒試料を得た。

【００２２】（実施例８）実施例６で用いたペロブスカイト型複合酸化物$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$粉末を$(La_{0.8}Sr_{0.2})(Co_{0.4}Fe_{0.6})O_3$粉末に代え、他は実施例６と同様の操作により実施例８の触媒試料を得た。

【００２３】（実施例９）実施例５で用いたペロブスカイト型複合酸化物$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$粉末を$La_{0.8}Ce_{0.2}CoO_3$粉末に代え、他は実施例５と同様の操作により実施例９の触媒試料を得た。

【００２４】（比較例）既に実用化されている自動車用触媒であるＰｔ－Ｒｈ／Al_2O_3触媒を比較例の触媒試料とした。Ｐｔ－Ｒｈ含有量は０．４３重量部であった。実施例及び比較例の組成を表１に示し、それぞれの触媒活性の測定結果を表２に示す。

【００２５】
【表１】

	ペロブスカイト型複合酸化物	Ｐｄ含有量（手順Ｃ）	溶液ｐＨ（手順Ｃ）	耐熱性酸化物	溶液ｐＨ（手順Ｅ）	総Ｐｄ量
実施例１	$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔0.55〕	1.8	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	1.8	Pd〔1.1〕
実施例２	$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔0.55〕	1.8	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	13.0	Pd〔1.1〕
実施例３	$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔0.55〕	13.0	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	1.8	Pd〔1.1〕
実施例４	$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔0.55〕	13.0	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	13.0	Pd〔1.1〕
実施例５	$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔1.1〕	1.8	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	——	Pd〔1.1〕
実施例６	$(La_{0.8}Ce_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔1.1〕	13.0	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	——	Pd〔1.1〕
実施例７	$(La_{0.8}Sr_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔0.55〕	13.0	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	13.0	Pd〔1.1〕
実施例８	$(La_{0.8}Sr_{0.2})(Co_{0.4}Fe_{0.6})O_3$〔50〕	〔1.1〕	13.0	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	——	Pd〔1.1〕
実施例９	$(La_{0.8}Ce_{0.2})CoO_3$〔50〕	〔1.1〕	1.8	$(Ce_{0.65}Zr_{0.30}Y_{0.05})O_2$〔50〕	——	Pd〔1.1〕
比較例				γ-Al_2O_3〔100〕	1.8	Pt-Rh〔0.43〕

〔　〕内の数値は重量部を表わす。

【0026】

【表2】

	初期50%浄化温度（℃）			耐久後50%浄化温度（℃）		
	CO	HC	NO	CO	HC	NO
実施例1	138	156	155	231	236	220
実施例2	131	151	151	220	226	218
実施例3	150	167	169	232	237	223
実施例4	141	164	170	226	233	218
実施例5	138	162	152	212	224	214
実施例6	132	166	168	231	240	216
実施例7	134	155	148	218	231	225
実施例8	130	160	155	227	241	234
実施例9	129	154	137	236	246	248
比較例	193	208	198	263	276	259

【0027】触媒活性の測定と耐久試験は以下のように行なった。

触媒活性の測定

ハニカム状（セル数400／inch²）コージェライト担体（直径30mm、長さ50mm）に担持されたそれぞれの試料を下記のモデルガスにて活性を測定した。ガス温度は触媒への入口ガス温度で示し、室温から昇温し、NO、CO、HC（$C_3H_6+C_3H_8$）のそれぞれが初期濃度の50%に低下した温度を50%浄化温度とする。また、リッチガスとリーンガスはそれぞれ1秒毎に切り換えた。触媒を通るガス流の空間速度（SV）は30，000／時間とした。

【0028】

	リッチガス	リーンガス
CO	2.6 %	0.7 %
HC（C_1換算濃度）	0.19%	0.19%
H_2	0.87%	0.23%
CO_2	8 %	8 %
NO	0.17%	0.17%
O_2	0.65%	1.8 %
H_2O	10 %	10 %
N_2	残部	残部

【0029】耐久試験

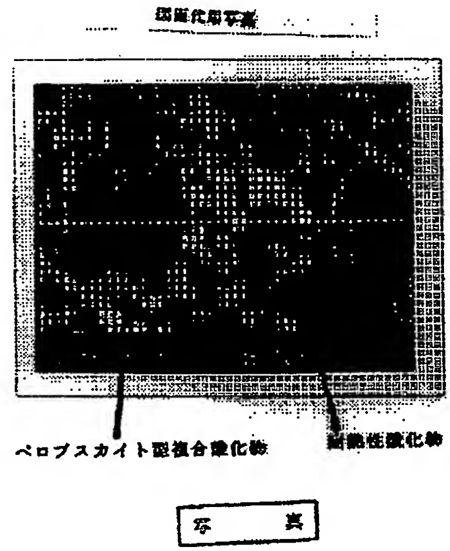
上記のリッチガスとリーンガスを5秒毎に切り換えて9

００℃で３０分、７５０℃で３０分のサイクルを１５回繰り返して耐久試験を行なった。耐久試験後にも前記の方法で触媒活性を測定した。表２の結果から明らかなように、各実施例では初期においても耐久後においても５＊
＊０%浄化温度が低く、比較例では高い。

【図面の簡単な説明】

【図１】実施例の触媒の金属組成とパラジウム分布を示す顕微鏡写真である。

【図１】



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